

Advantages of Combined Oxidants in Water Treatment

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Abstract

Combined oxidants use in water treatment has been increasing because of more stringent drinking water regulations. First of all, this paper will present a literature review of other studies concerning the advantages of combined disinfectants. This paper will also report on three laboratory and plant studies performed at two water plants in El Paso, Texas and a water plant in Aurora Colorado. All of these studies showed synergistic benefits of combined oxidants in reducing THMs and chlorite levels while increasing disinfection capability in the same disinfection zone and reducing bromate formation at the ozone water plant. The combined oxidants evaluated were chlorine dioxide and chlorine at the Canal Plant in El Paso; chlorine dioxide and chloramines treatment at Aurora Colorado Water Plant in reducing chlorite and THMs levels while increasing disinfection credit; and chlorine dioxide as a pre-oxidant to ozonation to reduce bromates in water with excessive bromide levels. Linear regression equations were developed from lab and plant studies to predict THMs formation and bromate formation. Combined chlorine dioxide and chlorine disinfection in the same zone showed the advantages of more chlorite reduction while increasing disinfection credit and providing a double barrier safety margin in the disinfection capability of the plant.

Key words: Oxidants; Combined Oxidants; Chlorine Dioxide; Chlorine, Ozone; Chloramines; TTHMs; Bromates; Disinfection.

Introduction

Gordon Finch, in the late 90's, showed synergistic disinfection benefits from sequential addition of chlorine dioxide and chlorine for *Cryptosporidium sp.* inactivation at lower CT levels than for chlorine dioxide alone (Figure 1). In the last 10 years, El Paso Texas and Aurora Colorado Plants have also shown the synergistic benefits in combining chlorine dioxide with chlorine in reducing chlorite levels and TTHMs levels in laboratory and plant studies. This new research and development on full plant scale is needed and timely because of the implementation of Stage 2 Disinfection and Disinfection By-Products Rule. With increasing disinfection requirements and lower disinfection byproduct levels, water plants will need treatment options that are more capable while being more cost effective. This paper will demonstrate this capability in using the combination of chlorine dioxide and chlorine in pretreatment; chlorine dioxide and chlorine in pretreatment with chloramines in the distribution system; chlorine dioxide pretreatment of

ozonation to lower bromates. Figure 2 shows the synergism of chlorine dioxide followed by monochloramine which is greater than with chlorine. A hypothesis suggests the increased effectiveness of interactive disinfectants is that the first oxidant (i.e., chlorine dioxide,) conditions the outer membrane of *Cryptosporidium oocysts* so that the secondary oxidant (i.e., chlorine or monochloramine) can penetrate the oocyst more easily(1,2,3).

Cryptosporidium Log-Kill by Snynergism of Cl₂ after 1.0 mg/l of ClO₂ for 45 minutes at pH 8 and 22° C

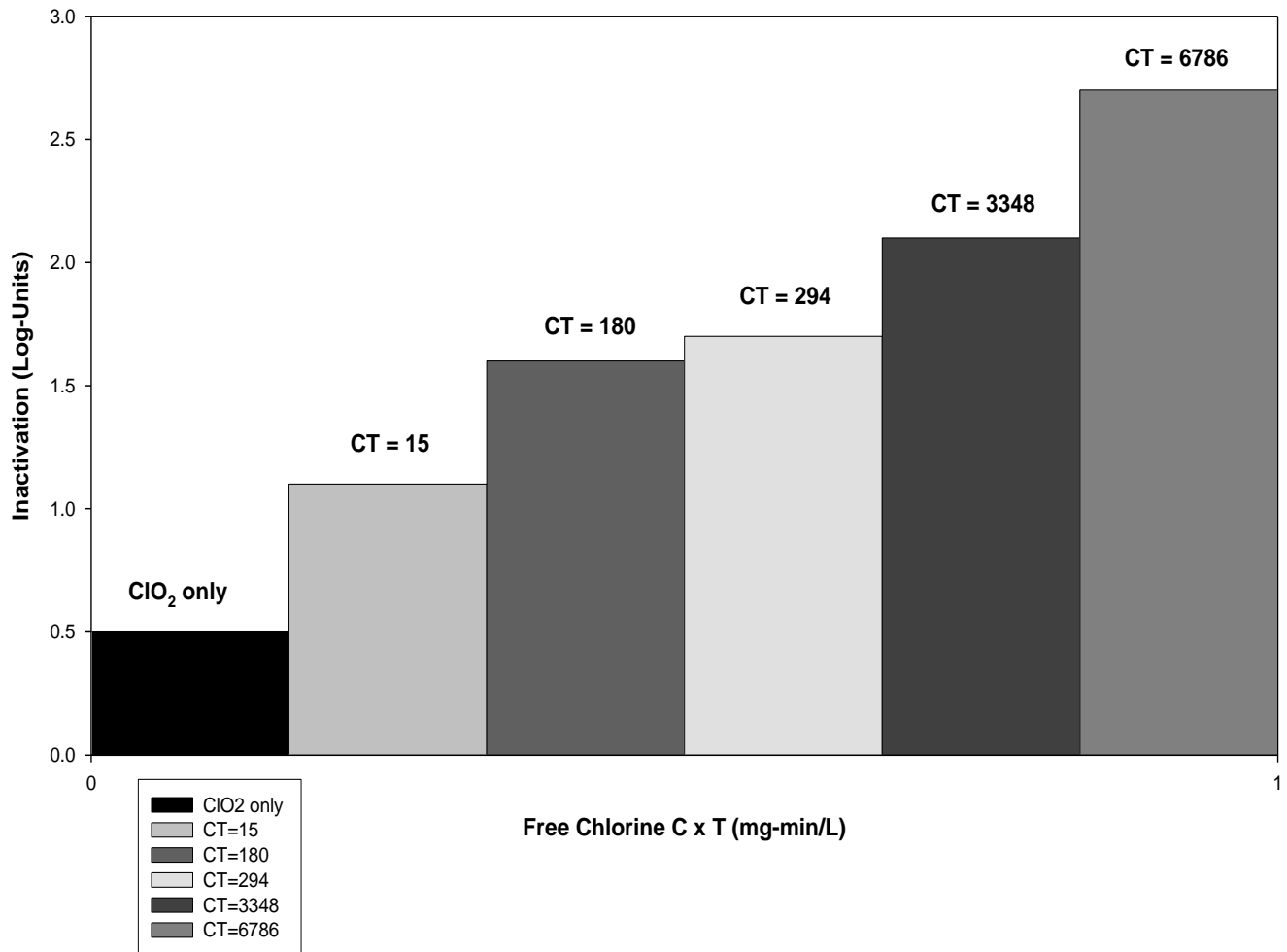


Figure 1 - Synergistic Disinfection Benefits from Chlorine Dioxide and Chlorine

***Cryptosporidium* Log-Kill caused by Synergism of Monochloramine
after 1.0 mg/L of ClO₂ for 45 minutes at pH 8 and 22^o C**

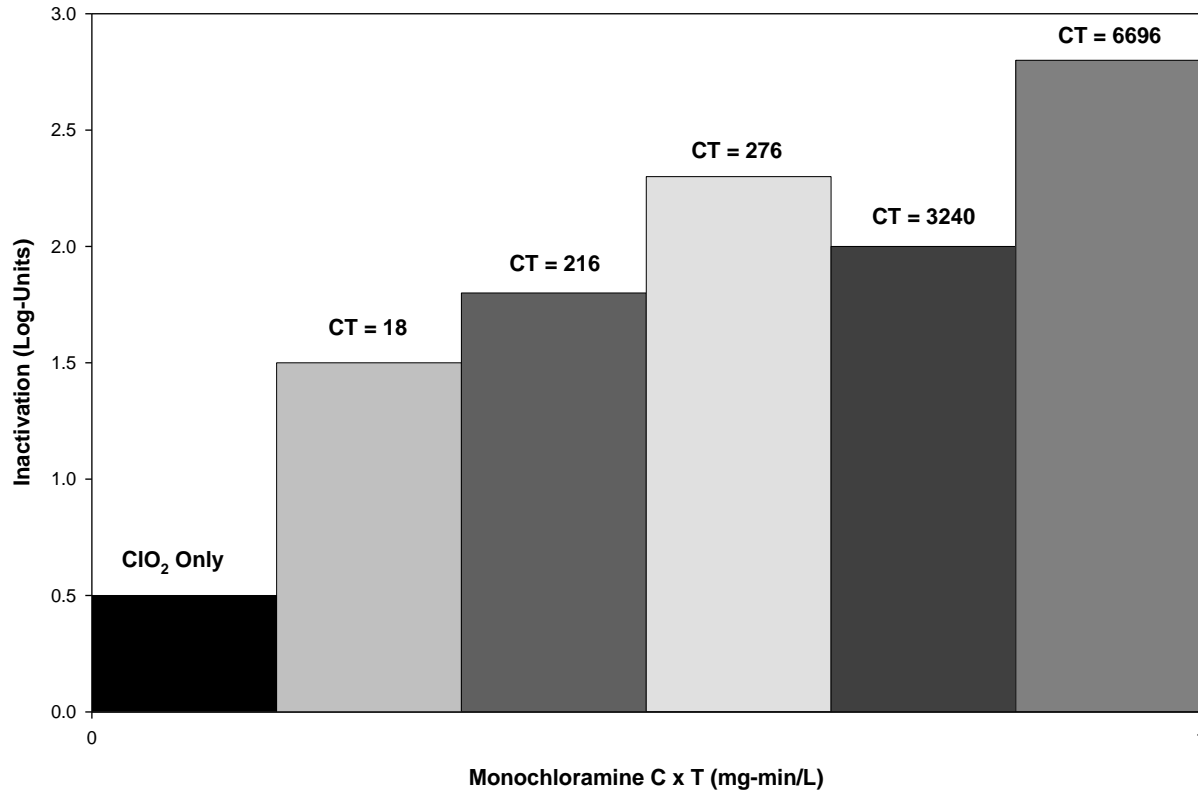


Figure 2 - Synergistic Disinfection Benefits from Chlorine Dioxide and Monochloramines

Reduction of Chlorite at Aurora, Colorado 80 MGD Wemlinger Water Plant

Aurora Colorado 80-mgd Wemlinger Water Treatment Facility was modified in 2002 by replacing chlorine with chlorine dioxide as the primary disinfectant. Chlorine dioxide use eliminated the need to construct new chlorine contact basins while meeting the Stage 2 Disinfectants and Disinfection byproducts Rule with a relatively small capital investment. Although the chlorine dioxide dose was not to exceed 1.4 mg/L in order to meet the 1.0 mg/L chlorite maximum contaminant level (MCL), the chlorite formation was 85% of the chlorine dioxide dose instead of the typical 70% maximum amount (Figure 3). Also, the decay rate of the chlorine dioxide was more rapid than expected. Therefore, the Wemlinger operations group faced the challenge of providing adequate CT while meeting the chlorite MCL goal. Based on Dr. Douglas Rittmann's research, the co-application of chlorine dioxide and chlorine could reduce the chlorite level and TTHM levels in the distribution system. Another benefit was that the co-application of chlorine and chlorine dioxide permitted both chemicals to satisfy the CT requirement in the same disinfection zone as approved by the Colorado Drinking Water Regulations.

When both chemicals are fed together, it was hypothesized that the chlorite byproduct from the chlorine dioxide reacted preferentially with the free chlorine to re-form chlorine dioxide while reducing the chlorite level to 73% of the chlorine dioxide dose from 80% to 85% observed at startup. Also, the chlorine satisfies some of the demand that was previously required for the chlorine dioxide. Bench-scale results demonstrated that a 1:1 ratio of chlorine to chlorine dioxide was ideal in reducing chlorite and TTHM levels in the distribution system(4).

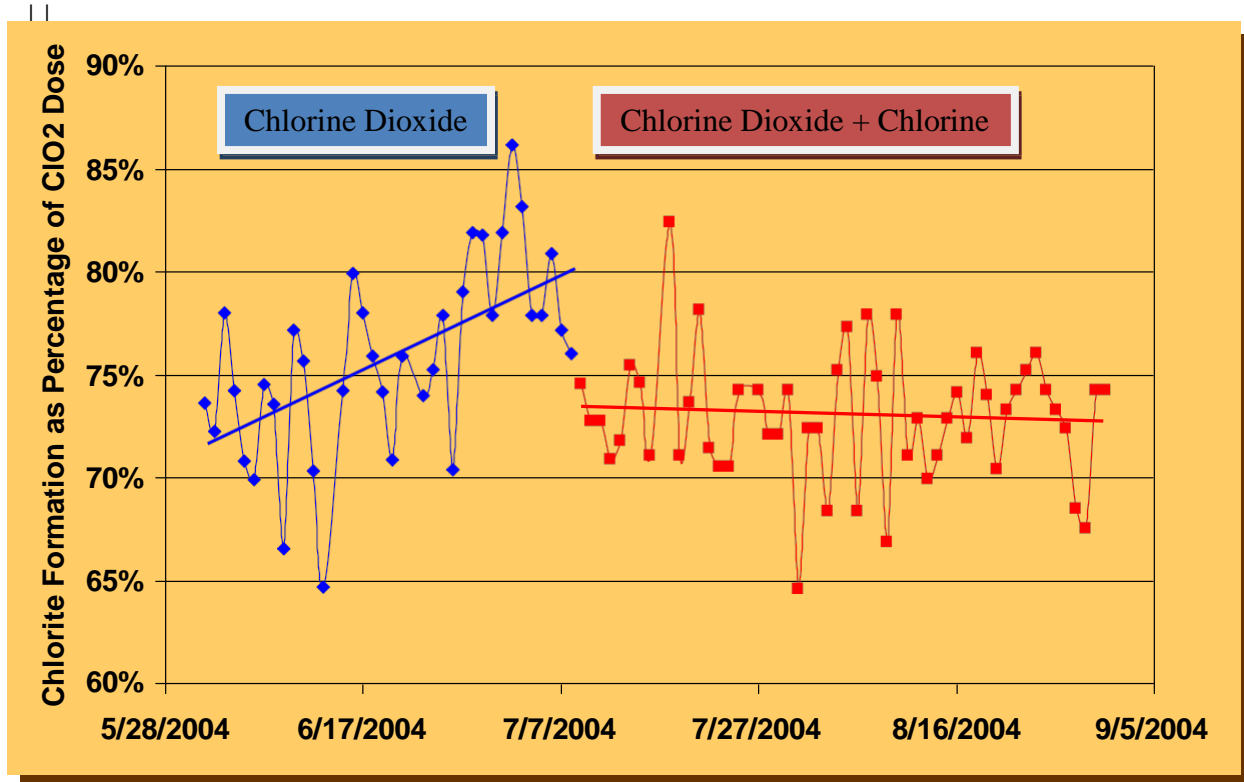


Figure 3 - Chlorite Reduction

Distribution TTHMs from Chlorine Only Treatment at Aurora Colorado

Table I reports the actual versus predicted TTHMs from chlorine only treatment during the period of February, 2001 to October, 2003 prior to the use of chlorine dioxide mixed with chlorine treatment at the Wemlinger Water Plant starting about May, 2004. The actual distribution system average THMs were 20.8 µg/L to 53.5 µg/L. The distribution system uses chloramination to minimize THM formation. Without pre-chlorination treatment, THMs were reduced to less than the Stage 2 maximum requirement but the plant needed to have a pre- disinfectant capability for additional safety from potential bacteriological breakthrough of the filters. Therefore, replacement of pre-chlorination with chlorine dioxide was determined a feasible alternative to pre-chlorination with the possibility of reducing TTHMs even more.

Figure 4 depicts table 1 data. A standard least squares JMP software model with effect leverage was used to determine predictive TTHMs based on the independent variables of finished water chlorine dosages, finished water pH levels, and finished water TOC levels. Although temperature and contact time are usually important variables in predicting TTHMs, they did not

have significant leverage on the results. The finished water temperatures for the samples were 6 degrees C to 16.6 degrees C which reflected a wide range of temperature conditions and certainly influenced the actual THMs to some extent. Also, the contact time would not have significant leverage to the predicted model likely due to the chloramination treatment in the distribution system as free chlorination would have in the El Paso Water System.

Table I – Distribution TTHMs Model Data Using Chlorine Only At Wemlinger Plant

Sample Number	Date	Distribution THM Average, µg/L	Predicted THM Average, µg/L	Residuals, µg/L	Final Cl ₂ Dose, mg/L	Finished Water TOC, mg/L	Finished Water pH
1	2/23/2001	20.8	23.7	- 2.9	3.7	1.27	7.43
2	4/20/2001	30	27.2	+2.8	3.8	1.48	7.44
3	9/19/2001	42.6	40.8	+1.8	4.2	1.99	7.73
4	11/12/2001	31.1	26.2	+4.9	4.2	1.36	7.45
5	1/11/2002	21.5	24.0	- 2.5	4.0	1.34	7.36
6	2/8/2002	22.4	24.2	- 1.8	4.0	1.30	7.41
7	3/8/2002	22.8	25.9	- 3.1	4.0	1.26	7.54
8	5/17/2002	26.3	26.1	+0.2	4.2	1.31	7.49
9	5/9/2003	47.7	50.8	- 3.1	5.2	2.8	7.51
10	6/13/2003	53.5	53.4	+0.1	8.0	2.69	7.51
11	9/22/2003	35.7	32.7	+3.0	4.3	1.9	7.34
12	10/6/2003	41.7	41.0	+0.7	5.2	2.3	7.39
	Maximum	53.5	53.4	+4.9	8.0	2.8	7.73
	Minimum	20.8	23.7	-3.1	3.7	1.26	7.34
	Average	33.0	33.0	.008	4.6	1.75	7.47

The whole model graph in figure 4 depicts the actual versus predicted TTHMs. The R-Square was excellent at 0.94 for the range of independent variables. The best leverage was TOC at P = 0.0005 while pH at P = 0.1008 and chlorine dose at P = 0.2734 are less significant. The lower the P value, the more significant the leverage on the dependent variable. The TTHM data average was 33 µg/L for the actual and predicted values with the residuals range from -3.1µg/L to + 4.9 µg/L, which is within the experimental error of THM analysis. The TTHMs predictive equation is as follows.

[1] Predictive Average Distribution TTHMs, µg/L = -133.5 + (1.5 * Final Cl₂Dose, mg/L) + (15.3 * Finished Water TOC, mg/L) + (17.8 * Finished Water pH).

Distribution TTHMs Using Chlorine Only at Wemlinger Plant

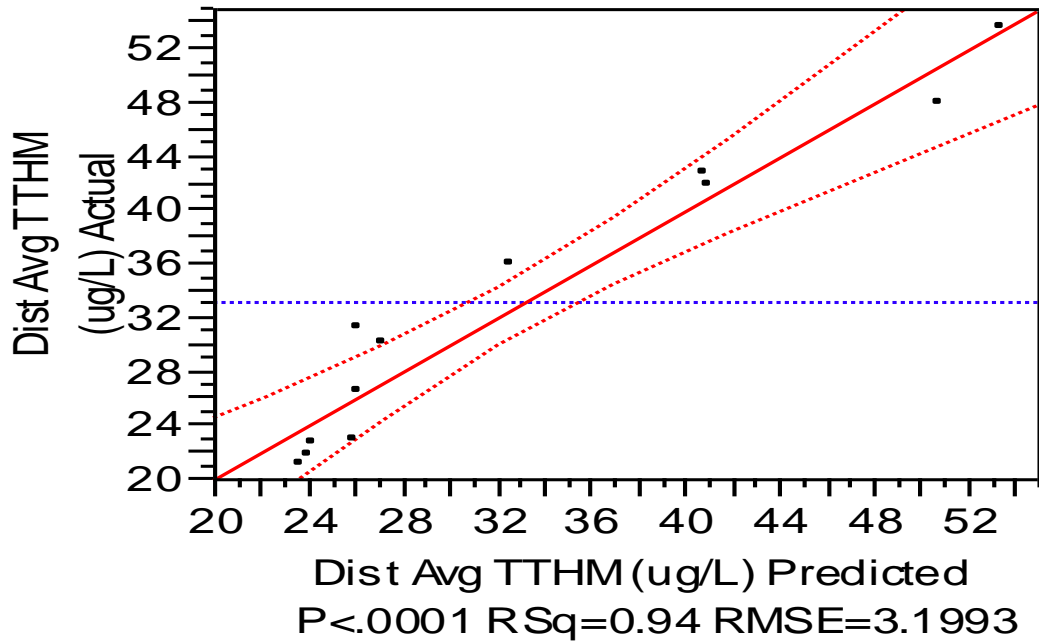


Figure 4- Actual versus Predicted THMs Model

Reduced TTHMs using Chlorine Dioxide with Chlorine at Wemlinger Water Plant

Figure 5 depicts Table II results on 23 samples of actual versus predicted TTHMs from chlorine dioxide combined with chlorine in pretreatment at Wemlinger Water Plant during the period of July, 2004 to October, 2008. The actual distribution system average TTHMs were 9.8 $\mu\text{g/L}$ to 26.3 $\mu\text{g/L}$ with an overall average of 16.4 $\mu\text{g/L}$. The chlorine dioxide dosages were 0.55 mg/L to 1.05 mg/L combined with chlorine dosages of 0.4 mg/L to 1.2 mg/L. The final pH levels of the water were 7.27 to 7.8 but had little leverage on the prediction model and therefore were not included in the equation. This was expected because the range of values was small and chloramines minimized their effect on TTHM formation. The water temperatures were 5.8 degrees C to 19 degrees C and the finished TOC levels were 1.18 mg/L to 3.2 mg/L but they had reduced effect on the model outcome which was, again, minimized by chloramination. However, they were included.

Table II – Actual THMS versus Predicted THMs using ClO₂ mixed with Cl₂

Sample	Date	Actual Dist. Average THM	Pred. Dist. Average THMs µg/L	Residuals, µg/L	ClO ₂ , mg/L	Cl ₂ Feed mg/L	Final Cl ₂ Dose mg/L	Finish pH	Finish Temp, C ^o	Finish TOC, mg/L
1	7/23/04	26.3	26.0	0.3	1.05	1	1.9	7.3	19	1.9
2	8/6/04	24.9	25.8	-0.9	1.05	1	1.95	7.38	18.4	2.5
3	9/10/04	25.4	25.1	0.3	1	0.85	2	7.32	17.7	3.2
4	10/8/04	23.8	23.6	0.2	1	0.85	2	7.45	15.6	1.96
5	3/11/05	13.7	14.7	-1.0	0.68	0.45	1.9	7.61	9	1.51
6	4/8/05	13.8	14.0	-0.2	0.65	0.43	1.95	7.62	10	1.66
7	6/10/05	21.9	21.6	0.3	0.9	0.75	2.1	7.29	16.6	2.57
8	9/9/05	18.1	18.3	-0.2	0.7	1	1.5	7.42	17.9	1.85
9	11/4/05	17.8	16.4	1.4	0.7	0.7	1.7	7.58	12.4	1.57
10	12/16/05	12.3	11.1	1.2	0.6	0.6	2	7.8	8.4	1.66
11	1/13/06	11.1	11.6	-0.5	0.6	0.6	1.9	7.59	7.3	1.63
12	2/10/06	12.6	13.8	-1.2	0.65	0.65	1.85	7.54	9.5	1.81
13	3/10/06	13.1	12.9	0.2	0.65	0.7	2	7.76	8.9	2.66
14	4/7/06	12.7	13.6	-0.9	0.65	0.7	1.95	7.62	11.6	1.75
15	5/5/06	11.3	12.4	-1.1	0.6	0.7	2.1	7.48	15	1.46
16	6/9/06	15.3	14.6	0.7	0.65	0.75	2	7.57	17	1.6
17	10/6/06	13.4	14.1	-0.7	0.7	0.9	2.15	7.79	15.4	2.05
18	11/3/06	13.4	13.0	0.4	0.7	0.9	2.1	7.76	11.5	1.61
19	6/8/07	20.3	20.6	-0.3	0.9	1.2	2	7.41	17	2.92
20	10/5/07	18.2	17.5	0.7	0.75	0.95	2	7.53	17.9	2.69
21	2/8/08	11.8	11.3	0.5	0.6	0.6	1.95	7.27	6.3	1.18
22	3/10/08	9.	9.4	0.4	0.55	0.7	1.9	7.53	5.8	1.32
23	10/10/08	15.6	15.2	0.4	0.7	0.4	2.35	7.4	14.3	2.01
Max.		26.3	26.0	+1.4	1.05	1.2	2.35	7.8	19	3.2
Min.		9.	9.4	-1.2	0.55	0.4	1.5	7.27	5.8	1.18
Avg.		16.4	16.4	0.10	0.74	0.76	1.97	7.52	13.1	2.00

The whole model graph in figure 5 depicts the actual versus predicted TTHMs. The R-Square value was excellent at 0.98 for the range of independent variables. The leverage was excellent for the chlorine dioxide dose ($P < 0.0001$), chlorine feed ($P = 0.008$), final chlorine dose ($P = 0.0005$), and water temperature ($P = 0.0006$) but the final TOC ($P = 0.2554$) had reduced effect. The pH effect was not significant because of the narrow range of values and the chloramines effect. The TTHM data average was $16 \mu\text{g/L}$ for the actual and predicted values which were about one half of the chlorination only model of $33 \mu\text{g/L}$. The residuals were $-1.2 \mu\text{g/L}$ to $+1/4 \mu\text{g/L}$ which, again, were within the experimental error of THM analysis. The predictive equation factors of the independent variables show two negative effects on THMs from chlorine feed and the final chlorine dose which may indicate the re-formation of chlorine dioxide by the reaction of free chlorine with the chlorite byproduct but the positive factor for chlorine dioxide dosage may indicate that the chlorine dioxide has a significant effect but not participating in oxidation of humic and fulvic acids (THMs) due to its low dosage and relatively short persistence in the water. The re-formation of chlorine dioxide may also slow the rate of THM formation until ammonia is added for chloramines treatment as compared to when free chlorine is only available. The chlorination only model also showed a greater positive effect on THMs from pH and TOC. Whatever is the exact cause of the lower THMs from combining chlorine dioxide and chlorine, the important fact is that 50% reduction is real and significant and should not be dismissed(5). The combined effect of chlorine dioxide and chlorine seems to enhance THM reduction at lower dosages too which was also shown in El Paso's bench-scale testing. The Wemlinger distribution TTHMs predictive equation 2 is:

[2] Predictive TTHMs, $\mu\text{g/L} = 4.90 + (27.6 * \text{ClO}_2, \text{mg/L}) + (-4.1 * \text{Cl}_2 \text{ feed, mg/L}) + (-5.5 * \text{Final Cl}_2 \text{ dose}) + (0.29 * \text{Final Temperature, C}^\circ) + (0.56 * \text{Final TOC, mg/L})$.

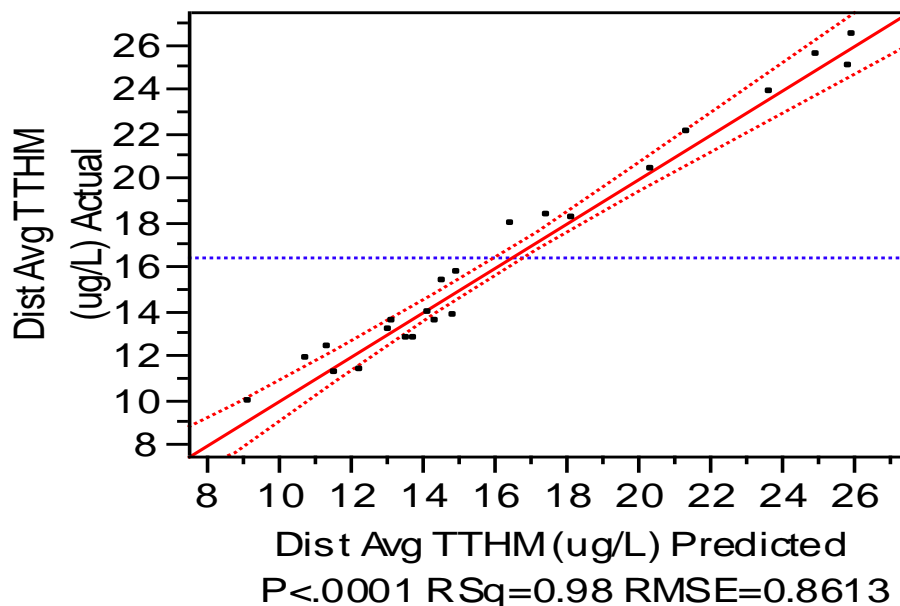


Figure 5 - Actual versus Predicted THMs for ClO_2 Mixed with Cl_2

Laboratory Bench-Scale Testing at El Paso Canal Water Plant

Analyses were performed at the El Paso Water Utilities Central Laboratory and an outside EPA approved laboratory using proper QC/QA procedures(6). The raw water source for the studies was the Rio Grande River, which was available for treatment normally during the period of March through September in El Paso, Texas. Chlorine dioxide solutions were added to Raw Rio Grande River from the Eka SVP-Pure Chlorine Dioxide Generator utilizing a two solution system containing 40% sodium chlorate/10% hydrogen peroxide (Purate™) and 78% sulfuric acid. In order to evaluate the impact of adding chlorine with chlorine dioxide on disinfection by-products, the raw water samples were dosed with 1, 2, or 3 mg/l of chlorine dioxide and dosed with various amounts of chlorine ranging from 0% to 200% of the chlorine dioxide dose. After the sample sets were initially dosed with chlorine dioxide and chlorine, they were held for about 45 minutes. Then, all of the sample sets were equally dosed with 7 mg/l of chlorine and held for 1-hour contact period in order to compare the effects of various ratios of chlorine dioxide and chlorine on TTHM formation (7).

Figure 6 shows the effect on TTHM formation of 1 mg/L of chlorine dioxide dosages (using a Eka Chlorate-Based Chlorine Dioxide Generator solution), spiked with chlorine doses ranging from 0% chlorine (chlorine dioxide only) to 200% chlorine dose of the chlorine dioxide dose.

The Figure 6 shows that the raw sample dosed with 7 mg/l chlorine alone, held for 1 hour contact time, forms about 42 ppb of TTHMs. The 1 mg/l chlorine dioxide dose with 0% chlorine had insignificant reduction in TTHMs. This is to be expected because the initial chlorine dioxide demand (< 1 minute time) of the Rio Grande River water is usually between 1.5 mg/l and 2.0 mg/l, i.e., there seems to be insufficient dosage to cause a long enough contact time of the chlorine dioxide with TTHM precursors to cause a significant reduction in TTHMs. However, when chlorine is added with the 1 mg/l of chlorine dioxide dose, the TTHM levels are reduced at the 33%, 66%, and 100% chlorine levels. At the 150% and 200% levels, the TTHMs are higher than the 0% chlorine and raw TTHM levels (chlorine only). The results imply that the chlorine with 1 mg/L chlorine dioxide is participating in TTHM reduction by possibly reforming chlorine dioxide with the chlorite by product during chlorine dioxide decay. Since most water plants dose at the 1 mg/L chlorine dioxide level, the reality is that chlorine dioxide at this concentration can “prevent” TTHM formation, but not reduce TTHMs compared to post chlorination treatment only. However, in this testing, it has been shown that TTHM reduction can be accomplished by adding chlorine with chlorine dioxide, even at the 1 mg/L dosage level compared to post chlorination treatment only. When the chlorite byproduct level is exceeded by the amount of the chlorine necessary to reform chlorine dioxide, the excess chlorine will participate in forming higher TTHMs. This also implies that chlorine is able to reduce the chlorite byproduct levels in order to re-form chlorine dioxide. As shown in figure 7, the chlorite and chlorate levels were analyzed at various % chlorine dosages to determine if chlorite was being reduced by the chlorine

1 mg/l Chlorine Dioxide & % Excess Chlorine Doses

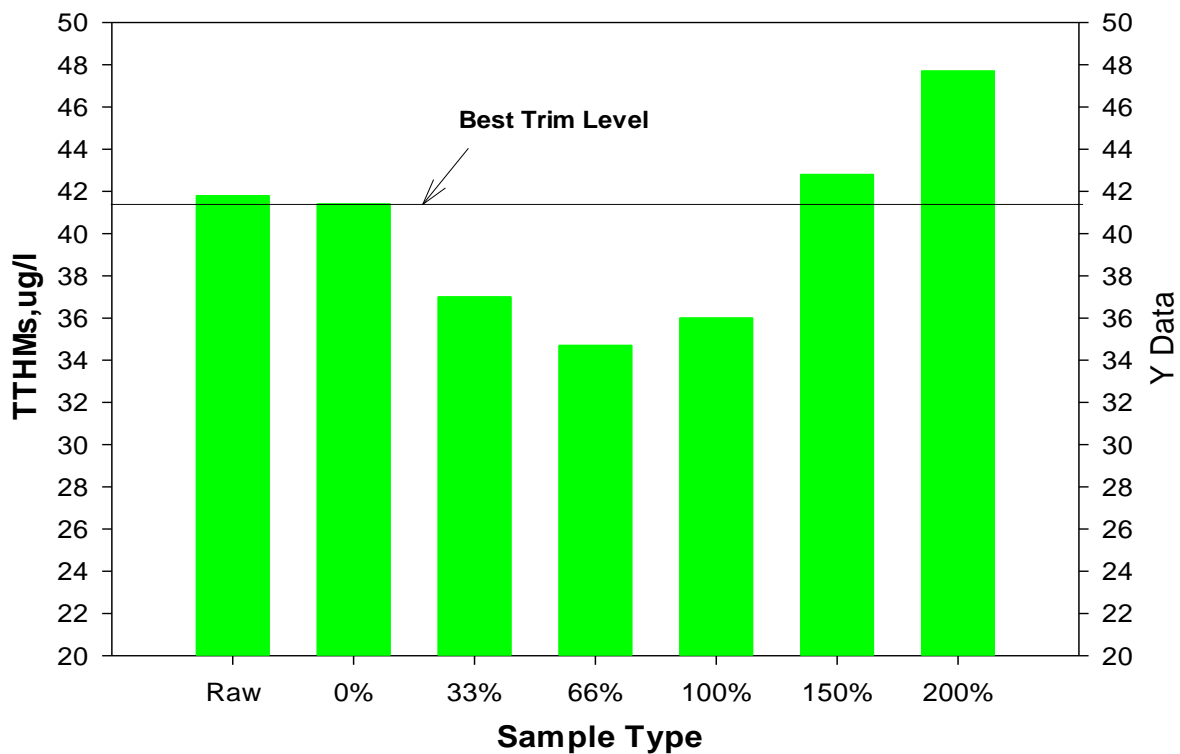


Figure 6 – Effect on TTHMs from 1 mg/L ClO₂ & Cl₂

In Figure 7 the chlorite and chlorate levels versus chlorine levels from 0% to 200% of the 1 mg/L chlorine dioxide dosages are plotted for the same samples depicted in Figure 6. At 0% chlorine (chlorine dioxide only), the chlorite level is highest at 0.46 mg/L while the chlorate level is 0.19 mg/L. As the chlorine dosages are increased, the chlorite levels decrease and the chlorate levels are rather flat throughout the range from 0% to 200% chlorine. The overall reduction in chlorite was about 0.10 mg/L (0.46 mg/L to 0.36mg/L). The chlorate level increase was negligible at about 0.03 mg/L (0.19 mg/L to 0.22 mg/L). Therefore, it seems reasonable that the chlorite reduction is principally caused by the sequence of reactions with chlorine to reform chlorine dioxide, ultimately being reduced to chloride. If the chlorine level exceeds the amount needed by the chlorite level for re-forming chlorine dioxide, the amount of the chlorine, not needed for chlorite oxidation, will participate in forming TTHMs. This may be the reason for the lowest TTHM level at about 66% chlorine and the subsequent increase in TTHMs at the 100%, 150%, and 200% chlorine dosages.

Excess Chlorine Effect on Chlorite & Chlorate at 1mg/l ClO₂

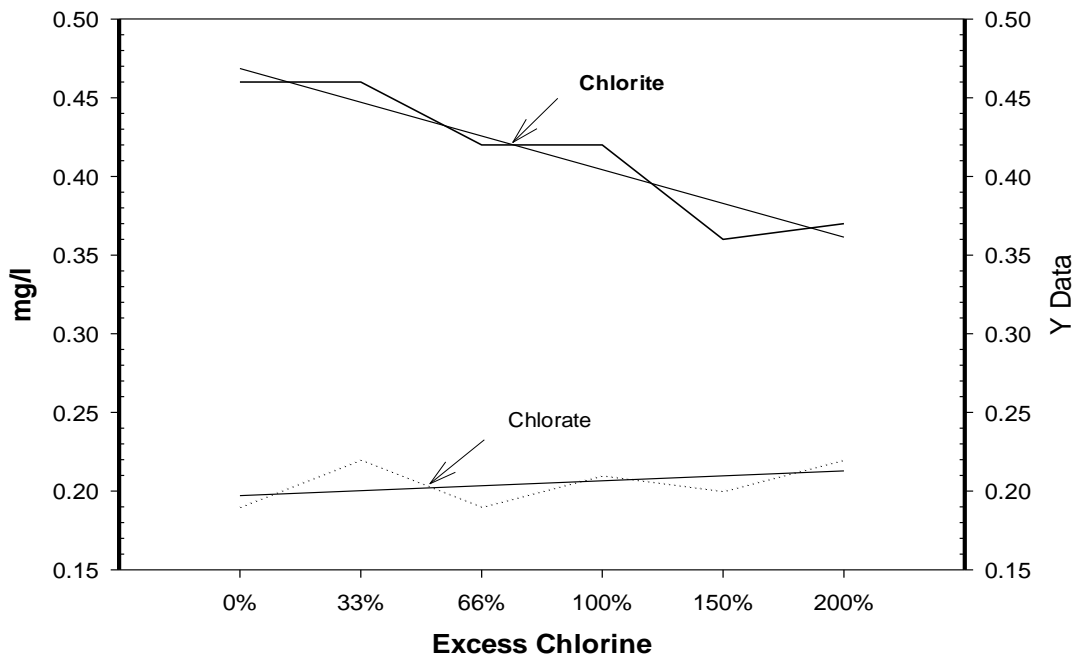


Figure 7 – Excess Chlorine Effect on Chlorite and Chlorate levels at 1 mg/L ClO₂ & Cl₂

Figure 8 shows the effect on TTHM formation of 2 mg/L of chlorine dioxide dosages with chlorine doses ranging from 0% chlorine to 200%. The 0% chlorine sample (chlorine dioxide only) shows a 15 ppb reduction of TTHMs from the raw TTHM level of 42 ppb. The 2 mg/L chlorine dioxide dose is apparently sufficient to exceed the immediate chlorine dioxide demand than the 1 mg/L dose. At the 33% and 66% chlorine doses, the TTHMs are reduced significantly more than the 1 mg/L chlorine dioxide dose with comparable chlorine levels, indicating that more chlorine dioxide is being formed from the reaction between the chlorite byproduct and free chlorine. As before, the 100%, 150%, and 200% chlorine dosages are showing increasing TTHM levels but lower than comparable chlorine levels with 1 mg/L chlorine dioxide doses.

2 mg/L Chlorine Dioxide & % Excess Chlorine Doses

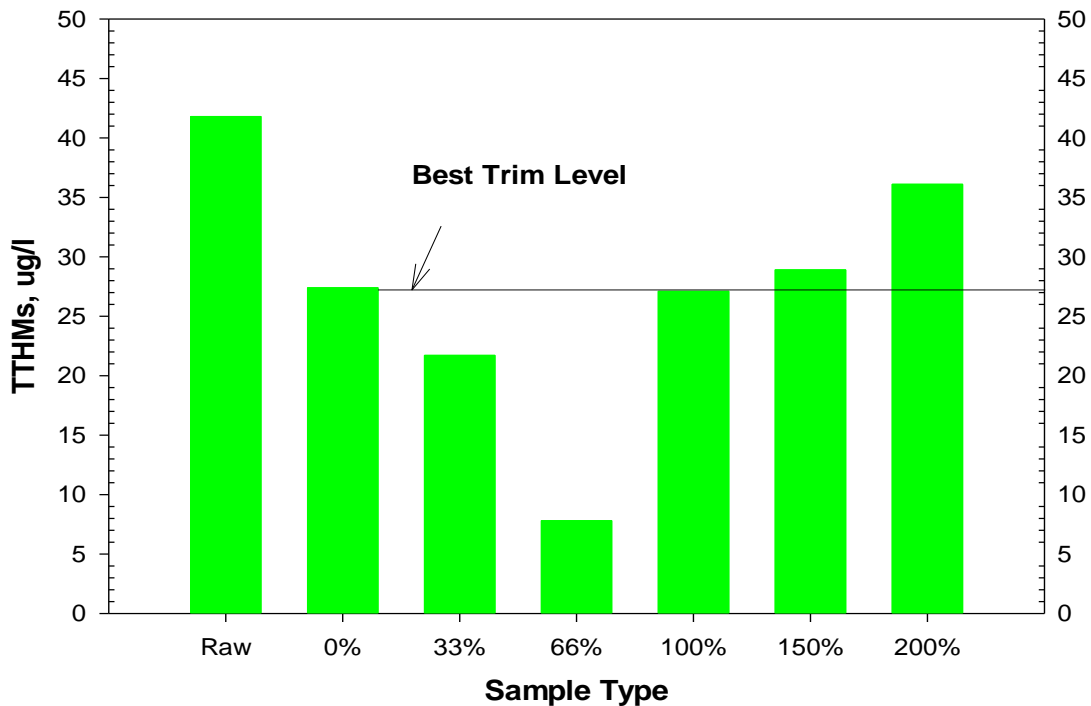


Figure 8 – Effect on TTHMs at 2 mg/L ClO_2 & Cl_2

Figure 9 shows the chlorite and chlorate levels plotted for chlorine levels from 0% to 200% for the same samples depicted in Figure 8. As before, the chlorite levels are decreasing while the chlorate level increases at a lower rate. The chlorite levels range from 0.90 to 0.69 or 0.21 mg/L difference as compared to the chlorate difference of 0.11 mg/L. The difference in the chlorite range of values is twice the amount compared to the 1 mg/L chlorine dioxide dose indicating that more chlorine dioxide re-formation is possible with the greater amount available from the higher chlorine dioxide dose. Therefore, the 2 mg/L chlorine dioxide dosages with chlorine reactions seem to have a similar consistent pattern as the 1 mg/L chlorine dioxide doses. The chlorate levels were determined to originate from the addition of chlorine in the hypochlorite solutions and not from the reaction of chlorine with the chlorite.

Effect of Excess Chlorine on Chlorite & Chlorate at 2 mg/l ClO₂

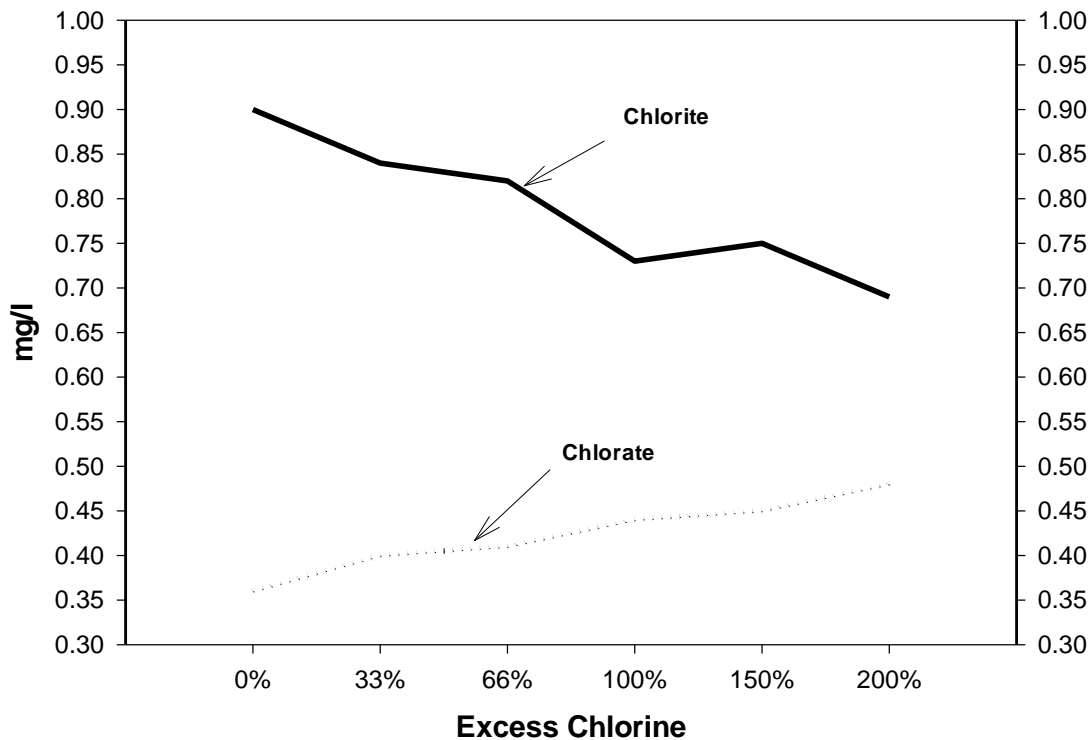


Figure 9 – Effect on Chlorite and Chlorate Levels at 2 mg/L ClO₂ & Cl₂

Model Equations for Cl₂ Only, ClO₂ Only, and Combined Cl₂ and ClO₂

Three model equations were developed to determine the effects of chlorine, chlorine dioxide, TOC, contact time, and pH on TTHMs in laboratory experiments at a constant temperature of 23 degrees C. Based on these model equations, figure 10 depicts the comparison of the results for the three conditions of 1). 7 mg/L chlorine dosage alone for 24 hours contact time, 2). 3 mg/L chlorine dioxide dosage alone for 1 hour contact time followed by 7 mg/L of chlorine dose for 24 hours contact time 3). 3 mg/L chlorine dioxide dosage mixed with 2 mg/L chlorine for 1 hour contact time followed by 7 mg/L chlorine dosage for 24 hours contact time. Samples were also pH adjusted from 5 to 9 prior to adding oxidants. The 7 mg/L chlorine dosage for 24 hours contact time calibrated well with the maximum TTHMs formed in the El Paso distribution system at various pH levels. Equation [3] below is the predictive equation for chlorine dosages alone.

$$[3] \text{ Predicted TTHMs, } \mu\text{g/L} = -201.6 + (0.87 * \text{Cl}_2, \text{ mg/L}) + (4.88 * \text{Time, hours}) + (4.27 * \text{TOC, mg/L}) + (27.69 * \text{pH}).$$

The ranges of the independent variables for the chlorine alone model were as follows: 1). chlorine dosages were 2 mg/L to 100 mg/L, 2). pH levels were from 5 to 9; 3). TOC levels were 2.8 to 5.9 mg/L, and 4). contact times were 1 hour and 24 hours. There were 27 samples analyzed with an R- square of 0.94. The leverage effect was significant (P = <0.0005) from chlorine, contact

time, and pH but had a reduced effect from TOC (P= 0.4931)

The chlorine dioxide only model predicted THM results based on 3 to 7.5 mg/L chlorine dioxide dosages at 1 hour contact time followed by chlorine dosages of 2 to 7 mg/L at contact times of 1 hour and 24 hours, for pH levels from 5 to 9, and TOC concentrations ranging from 2.8 to 5.3 mg/L. Seventeen samples were analyzed. The whole model equation was as follows:

$$[4] \text{ Predicted THMs, } \mu\text{g} = -89.4 + (-11.2 * \text{ClO}_2, \text{ mg/L}) + (4.1 * \text{Cl}_2, \text{ mg/L}) + (3.8 * \text{Time, hours}) + (-11.4 * \text{TOC, mg/L}) + (21.8 * \text{pH}).$$

The R square was excellent at 0.94 with a mean of response of 60.5 ppb THMs and all independent variables had significant leverage (P = <0.0005). The negative factors for chlorine dioxide dose and TOC of -11.2 ppb and -11.4 ppb per mg/L, respectively, showed the oxidation potential of chlorine dioxide in reducing THM precursors (humic acid and fulvic acid) because, in these experiments, the TOC was not removed by coagulation or filtration, i.e., each raw sample was dosed only with the oxidants.

The combined chlorine dioxide and chlorine dosages were generated in a Rio Linda Chlorine dioxide generator (25% chlorite with chlorine gas) by over-feeding the chlorine up to 75% over the best trim setting for chlorine dioxide generation. Twenty sample runs were performed under the following test conditions: 1). chlorine dioxide dosages were 3 to 7.5 mg/L, 2). The chlorine dosages added for TTHM formation potential were from 0 to 100 mg/L, 3). The chlorine contact times were 1 hour and 24 hours, 4). The TOC concentrations were 2.6 mg/L to 5.1 mg/L, 5). The pH levels were adjusted from 5 to 9 prior to adding the oxidants.

$$[5] \text{ The predicted TTHMs, } \mu\text{g/L} = -154.0 + (-1.63 * \text{ClO}_2, \text{ mg/L}) + (0.60 * \text{Cl}_2, \text{ mg/L}) + (3.61 * \text{Time, hours}) + (14.4 * \text{TOC, mg/L}) + (12.74 * \text{pH units}).$$

The R-square was equal to 0.95 with a mean response of 64.4 ppb. The leverage was significant (P = <0.05) for the independent variables except the chlorine dioxide dose had a reduced effect (P = 0.3133). The factors for the chlorine, and pH were significantly lower compared to the chlorine dioxide only model. The whole model equation predicted TTHMs at about 1/3 of the chlorine only model and about one half of the chlorine dioxide model. The rate of TTHM reduction per mg/L of chlorine dioxide was 18 ppb with 1:0.66 ratio of dosages compared to 8 to 10 ppb per mg/L of chlorine dioxide dose in the chlorine dioxide only model. The Wemlinger Plant's rate of TTHM reduction per mg/l was 22 ppb at a ratio of 1:1 chlorine dioxide to chlorine dosages.

In figure 10, the raw water dosed with 7 mg/l of chlorine only condition had a 28 $\mu\text{g/L}$ TTHM increase per pH unit ranging from 81 ppb at pH 5 to 192 ppb TTHMs at pH 9. The 3 mg/L chlorine dioxide dose only condition with 7 mg/L finished water chlorine dose had 20 $\mu\text{g/L}$ increase of TTHMs per pH unit ranging from about 62 ppb at pH 5 to 142 ppb TTHMs at pH 9. The 3 mg/L chlorine dioxide dose mixed with 2 mg/L of chlorine condition followed by 7 mg/L finished water chlorine dose had 10 ppb increase per pH unit ranging from 54 $\mu\text{g/L}$ at pH 5 to 95 ppb at pH 9. This last treatment scenario was chosen as the preferred option for full scale operation. In the early 1990's, based on Mark Griese's and Iatrou's papers concerning chlorite reduction by ferrous ion, El Paso began using ferrous chloride to reduce excessive chlorites from a

2.5 mg/L chlorine dioxide dose(8,9). However, in 1999, El Paso decided to increase the chlorine dioxide dose to 3.0 mg/L mixed with 2 mg/L of chlorine in order to reduce TTHMs further. The plant has been able to meet the Stage 2 Disinfection/Disinfection By-Product Rule requirements with the 3 mg/L chlorine dioxide dose mixed with 2 mg/L chlorine dose at finish water pH 7.0 as predicted in figure 10 below(10).

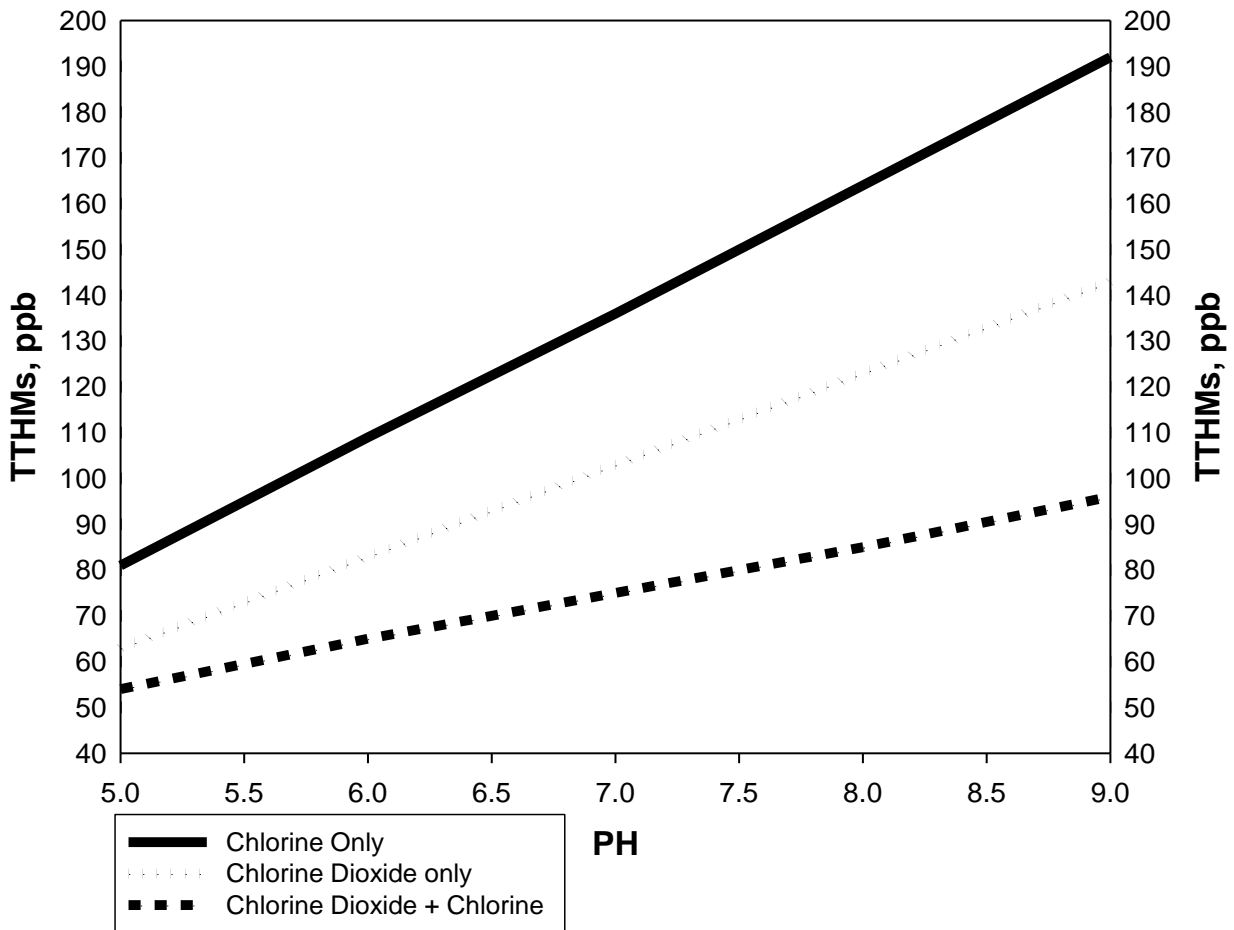


Figure 10 - The Effects on TTHMs from Chlorine, Chlorine Dioxide and Mixture

Bromate Reduction from Chlorine Dioxide Pretreatment of Ozone

The 60 MGD Jonathan Rogers Water Plant treats Rio Grande River Water during the months of March through October. The raw water is lifted into 5 storage ponds by three screw conveyor pumps. After initial settling of turbidity in the storage pond, the settled water pumps lift the water into the plant treatment trains where a small dose of ozone is added to reduce some taste and odors and reduce coagulant dosages by micro-flocculation action. Bromates are not formed at this point due to the low ozone dosage. The ferric chloride coagulant is then added to reduce the turbidity and TOC levels through mixing and sedimentation processes. The original plant design specified excess lime treatment with the ferric chloride followed by re-carbonation at the end of sedimentation to lower the pH level. However, since excess lime and re-carbonation are no longer needed, the re-carbonation chamber is an ideal location for chlorine dioxide addition because the detention time permits complete decay of the chlorine dioxide species prior to entering the first ozone cell contactor. Since the Contra Costa Study showed that the chlorite residual was the significant species in preventing bromate formation, it may be also important to minimize chlorate formation by reducing the chlorine dioxide species level prior to entering the ozone contactor and only forming chlorates from the reaction of ozone with the chlorite by-product. Previous studies on the Rio Grande River showed each mg/L of chlorine dioxide formed about 0.67 mg/L of chlorite byproduct. Therefore, it was expected that about 0.67 mg/L of chlorates would be in the effluent from a 1 mg/L chlorine dioxide dose. After chlorine dioxide addition, ozone is added to the first cell of the Pre-Filtration Ozone Contactor to obtain disinfection credit based on the ozone residual times the contact time (CT). The pH of the water entering the ozone contactor is about 7.3. As the water passes from the first cell into the second cell, then, about 1 mg/L of hydrogen peroxide is added to react with the ozone residual forming peroxone which reduces taste and odors from geosmin, MIB, and pyrazine and prevents additional bromate formation. The Plant Operators set the ozone dose to at least 0.3 mg/L ozone residual in the first cell for inactivation of *Giardia sp.* However, the bromates are also formed from the reaction of bromide with the ozone. After peroxone treatment, the water passes through biological granular activated carbon (GAC) filters, where turbidity is reduced to less than 0.1 ntu and more total organic carbon (TOC) is removed. After filtration, chlorine and phosphate chemicals are added to further disinfect the water and prevent corrosion, respectfully, within the distribution system.

2005 Plant Study of Ozone and Chlorine Dioxide Dose Effects on Bromates

Figure 11 and Table III show the results of the 2005 Plant Study of ozone and chlorine dioxide effects on bromate formation. The results of 41 observations listed in Table III with a mean of response of 2.9 µg/L has a range of bromate levels of 1 µg/L to 13 µg/L. The actual minus predictive values were equal to -1.4 µg/L to +1.6 µg/L. The range of contact times per contactor were 3.26 minutes (10.14 MGD rate) to 5.63 minutes (5.825 MGD rate). The range of the ozone residuals were 0.2 mg/L to 0.65 mg/L. The highest bromate level of 13 µg/L exceeded the MCL because of insufficient chlorine dioxide dose of 0.44 mg/L while the second highest bromate level of 10 µg/L had an insufficient chlorine dioxide dose of 0.73 mg/L for the contact time of 5.0 minutes (6.55 MGD rate). The longest contact time of 5.63 minutes (5.825 MGD) and

highest ozone residual of 0.65 mg/L with a high chlorine dioxide dose of 1.4 mg/L exemplified the best capability of the chlorine dioxide at a 9.0 µg/L bromate level.

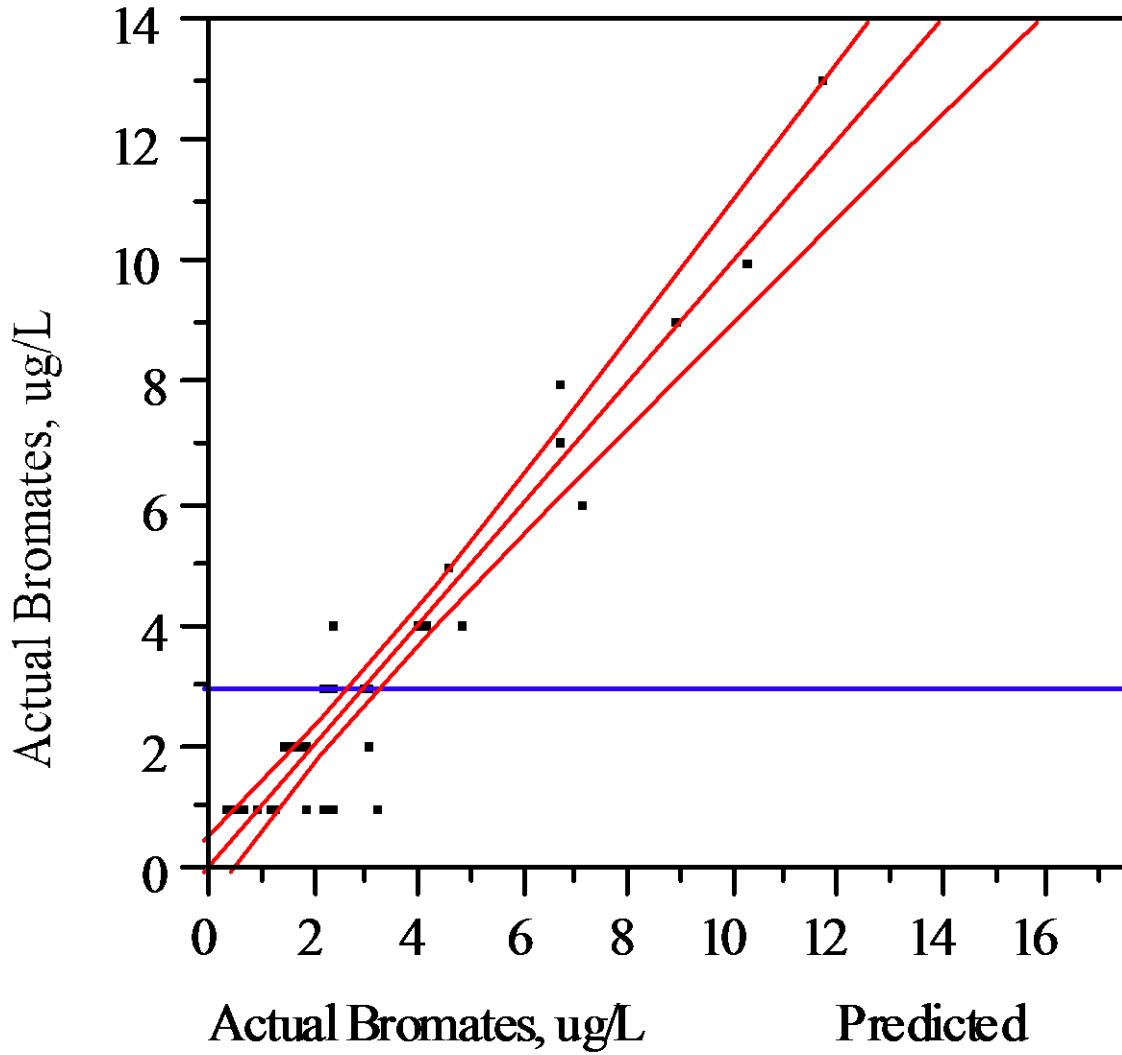


Figure 11- 2005 Plant Study of Ozone and Chlorine Dioxide Effects on Bromate Formation

Table III. 2005 Plant Study of Chlorine Dioxide and Ozone Effects on Bromates

#	Flow, MGD	O ₃ Res, mg/L	Time, min.	ClO ₂ , mg/L	Actual BrO ₃ , µg/L	Pred BrO ₃ , µg/L	Actual – Predict
1	9.91	0.23	3.30	1.28	1.0	0.5	+0.5
2	9.91	0.23	3.30	1.28	1.0	0.5	+0.5
3	9.05	0.27	3.55	1.40	1.0	0.7	+0.3
4	10.04	0.2	3.28	1.26	1.0	0.4	+0.6
5	10.04	0.2	3.28	1.26	1.0	0.4	+0.6
6	9.95	0.28	3.29	1.23	1.0	1.0	0.0
7	9.33	0.31	3.45	1.31	1.0	1.2	-0.2
8	9.33	0.31	3.45	1.31	1.0	1.2	-0.2
9	9.72	0.26	3.35	1.33	1.0	0.5	+0.5
10	9.72	0.26	3.35	1.33	1.0	0.5	+0.5
11	7.29	0.36	4.46	1.67	3.0	2.3	+0.7
12	7.29	0.36	4.46	1.67	1.0	2.3	-1.3
13	7.27	0.38	4.47	1.67	1.0	2.4	-1.4
14	7.27	0.38	4.47	1.67	1.0	2.4	-1.4
15	7.3	0.45	4.45	1.74	3.0	2.3	+0.7
16	7.3	0.45	4.45	1.74	3.0	2.3	+0.7
17	8.4	0.485	3.82	0.73	8.0	6.7	+1.3
18	8.4	0.485	3.82	0.73	7.0	6.7	+0.3
19	8.13	0.31	3.95	1.09	4.0	4.0	0.0
20	8.13	0.275	3.95	1.23	3.0	3.0	0.0
21	9.135	0.385	3.52	1.10	2.0	3.1	-1.1
22	9.135	0.385	3.52	1.10	3.0	3.1	-0.1
23	6.54	0.41	5.01	1.67	4.0	4.2	-0.2
24	6.54	0.41	5.01	0.44	13.0	11.7	+1.3
25	6.55	0.485	5.00	0.73	10.0	10.3	-0.3
26	8.14	0.5	3.95	0.73	6.0	7.2	-1.2
27	8.33	0.305	3.85	1.45	2.0	1.5	+0.5
28	8.33	0.305	3.85	0.94	5.0	4.6	+0.4
29	7.98	0.365	4.03	1.53	2.0	1.9	+0.1
30	7.98	0.365	4.03	1.53	2.0	1.9	+0.1
31	8.785	0.405	3.65	1.40	2.0	1.7	+0.3
32	8.785	0.405	3.65	1.40	2.0	1.7	+0.3
33	8.23	0.325	3.90	1.44	2.0	1.8	+0.2
34	8.23	0.325	3.90	1.44	2.0	1.8	+0.2
35	8.19	0.15	3.92	0.80	4.0	4.9	-0.9
36	8.19	0.32	3.92	1.53	1.0	1.3	-0.2
37	7.41	0.255	4.38	1.53	4.0	2.4	+1.6
38	7.41	0.255	4.38	1.53	3.0	2.4	+0.6
39	7.67	0.345	4.21	1.60	1.0	1.9	-0.9
40	7.67	0.345	4.21	1.60	1.0	1.9	-0.9
41	5.825	0.65	5.63	1.40	9.0	8.9	+0.1

Summary Table Results of 2005 Plant Study based on Predictive Equations for Ozone and Chlorine Dioxide Effects on Bromate Formation

Table IV show the bromate levels for 3.25 minutes to 6.5 minutes (5 to 10 MGD rates per contactor) at ozone residuals of 0.3 mg/L with three chlorine dioxide doses compared to ozone alone. Equations 6 and 7 below determine the bromate levels from ozone alone and chlorine dioxide pre-oxidation of ozone, respectively.

[6], Bromates, $\mu\text{g/L} = -43.75 + (68.60 \times \text{Ozone Residual, mg/L}) + (7.46 \times \text{Contact time, minutes})$, was used for the ozone only calculations and

[7] Bromates, $\mu\text{g/L} = -1.95 + (4.01 \times \text{ozone residual, mg/L}) + (2.98 \times \text{time, minutes}) + (-6.35 \times \text{Chlorine Dioxide, mg/L})$, was used for the chlorine dioxide pre-oxidation of ozone.

Table IV shows that the 0.5 mg/L chlorine dioxide dose with 0.3 mg/L ozone residual was insufficient to reduce bromates to less than 10 $\mu\text{g/L}$ MCL at contact times greater than 5.4 minutes (<6.0 MGD flow). However, shorter contact times (or higher flow rates) and higher chlorine dioxide doses were effective. The 1.0 mg/L chlorine dioxide dose was similarly ineffective at the contact time of 6.5 minutes (5.0 MGD) but was effective at reducing bromates at shorter contact periods with higher flow rates >6.0 MGD. Only the 1.5 mg/L chlorine dioxide dose was consistently capable of lowering bromates to less than 10 $\mu\text{g/L}$ MCL at 5.0 to 10.0 MGD flow rates by an average of 73 per cent. Ozone alone can comply with the bromate MCL for flow rates from 8 to 10 MGD per contactor but chlorine dioxide is needed for lower flow rates(12,13).

Table IV. Bromate Formation for 3 Chlorine Dioxide Doses and Ozone only at 0.3 Ozone Residual in Plant Study

Flow, MGD	Time, minutes	Ozone Residual, mg/L	1.5 mg/L ClO ₂ Dose, mg/L	1.0 mg/L ClO ₂ dose, mg/L	0.5 mg/L ClO ₂ dose, Mg/L	Ozone only	% Reduction Range
5.0	6.5	0.3	9.1	12.3	15.4	25.3	39 to 64
6.0	5.4	0.3	5.8	9.0	12.2	17.1	29 to 79
7.0	4.64	0.3	3.6	6.7	9.9	11.4	13 to 68
8.0	4.06	0.3	1.8	5.0	8.2	7.1	0 to 75
9.0	3.61	0.3	<1.0	3.7	6.8	3.8	0 to ~80
10.0	3.25	0.3	<1.0	2.6	5.8	<1.0	0

Conclusions

The following conclusions can be made with reasonable certainty:

1. The Wemlinger Plant in Aurora Colorado has shown through bench-scale and plant studies that the chlorite level can be reduced by mixing chlorine and chlorine dioxide.
2. The TTHM system data average was 16 $\mu\text{g/L}$ with combined chlorine dioxide and chlorine dosages at 1:1 ratio for the Wemlinger Plant, which was about one half of the chlorine only TTHM distribution system average of 33 $\mu\text{g/L}$.
3. The TTHM reduction was 22 $\mu\text{g/L}$ per mg/L of chlorine dioxide mixed with chlorine at 1:1 ratio from Wemlinger Plant compared to El Paso Canal Plant's 18 $\mu\text{g/L}$ per mg/L of chlorine dioxide mixed with chlorine at 1:0.66 ratio.
4. El Paso bench-studies showed that 1 mg/L ClO_2 dose to raw water had no reduction in TTHM formation potential but 1 mg/L ClO_2 mixed with 0.66 mg/L Cl_2 reduced TTHMs formation potential by 19%.
5. El Paso bench-scale studies showed that chlorine dioxide mixed with chlorine at a ratio of 1:0.66, respectively, is optimum for THM reduction.
6. El Paso lowered TTHMs at the rate of 18 $\mu\text{g/L}$ per mg/L chlorine dioxide mixed with chlorine in the range of 3 to 7.5 mg/L of chlorine dioxide dose compared to 8 to 10 $\mu\text{g/L}$ per mg/L when chlorine dioxide only is used.
7. The combined chlorine dioxide and chlorine whole model equation predicted TTHMs at about one third of the chlorine only model and about one half of the chlorine dioxide only model in El Paso.
8. The plant study at the JRWTP predicted accurately the effect of ozone residual, contact time, and chlorine dioxide dose on bromate formation.
9. Bromates were reduced by 6.34 $\mu\text{g/L}$ per mg/L of chlorine dioxide dose in the plant study.
10. Chlorite residuals were consistently less than 0.01 mg/L after ozonation with chlorine dioxide doses of 0.5 mg/L to 1.5 mg/L in the plant study.
11. Average chlorate level was 62% of the applied chlorine dioxide dose in the plant study.
12. Ozone alone can comply with the 10 $\mu\text{g/L}$ bromate MCL at contact times of 4.06 minutes or less (>8.0 MGD rate per contactor) with 0.3 mg/L ozone residual.
13. The 0.5 mg/L chlorine dioxide dose at 0.3 mg/L ozone residual was insufficient to reduce bromates at contact times greater than 4.06 min (<8.0 MGD flow).
14. The bromate reduction for ozone residuals at 0.3 mg/L was about 78% at 1.5 mg/L chlorine dioxide dose. However, the Contra Costa study showed 78% reduction at 1.0 mg/L chlorine dioxide dose but had a lower total organic carbon treatment level of 2.0 mg/L compared to El Paso's 3.0 mg/L level. Perhaps, TOC levels may affect % reduction of bromates by chlorine dioxide.

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